Special Feature 2001

Quantum Chemistry/Molecular Dynamics Simulations of Condensed Phase Spectra

Joel D. Kress (T-12), Thomas D. Sewell (T-14), Lee A. Collins (T-4), and Edward M. Kober (T-14)

The combination of rapid increases in computational hardware and improved quantum chemistry software tools is beginning to enable dynamical simulation of condensed phase molecular systems without the need to parameterize a classical force field. These quantum chemistry/molecular dynamics (QC/MD) methods, in which the classical phase space trajectory for nuclear motion in a molecular system is propagated in time using forces derived directly from the electronic wave function *via* the Hellmann-Feynman theorem, offer significant advantages over traditional molecular dynamics methods:

- Elimination of the requirement to formulate and/or parameterize an empirical force field for each system of interest.
- Implicit inclusion of chemical reactivity, subject to proper treatment of spin states and the inherent accuracy of the theoretical model and basis sets used.
- Determination of dynamic properties such as the system dipole moment vector or polarizability tensor directly from the electron density.
- Each of the preceding at arbitrary pressures and temperatures.

Although practical considerations still limit most QC/MD simulations to studies of systems containing hundreds of atoms for times of picoseconds or less, this is sufficient to allow calculations of various properties of interest, such as:

- Infrared, Raman, or inelastic neutron scattering spectra.
- Energy transfer rates and pathways in shocked materials.
- Reaction paths and energetics in condensed phases.

Calculation of spectra for comparison to experiment is one means of validating a chosen theoretical model and basis set, prior to its use in subsequent, more sophisticated simulations.

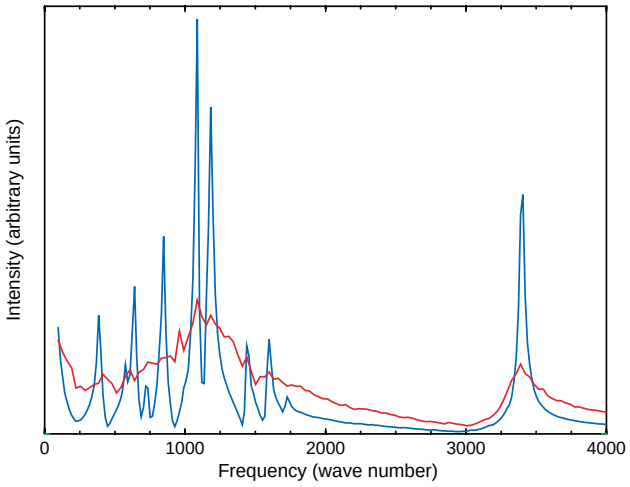

Figure 1: Simulated inelastic neutron scattering spectrum for room temperature (blue and compressed (red, pressure = 9 GPa) benzene.

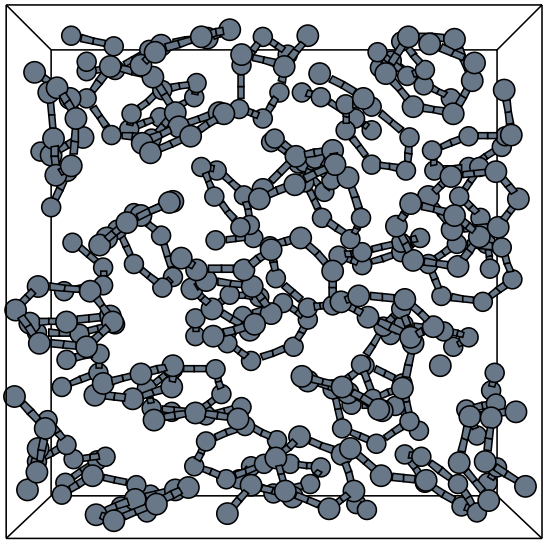

Figure 2: Quantum chemistry/molecular dynamics snapshot of compressed benzene. (54 molecules, hydrogen atoms are omitted for clarity.)

For example, the infrared spectrum is given by

$$I(\omega) \propto \int_0^T d\tau' \exp(i\omega\tau) \langle \vec{\mu}(\tau) \cdot \vec{\mu}(0) \rangle,$$

where the quantity in brackets is the normalized time autocorrelation function of the system dipole moment vector, given in turn by

$$\vec{\mu}(t) = -\int_{-\infty}^{\infty} d^3\vec{r}\rho[\vec{r}(t)] \cdot \vec{r}(t) + {}_{nuclei} Z_i \vec{R}_i(t).$$

This latter integral over the instantaneous electron density distribution of the system is clearly a nonclassical quantity.

By contrast, the inelastic neutron scattering (INS) spectrum, which corresponds to incoherent scattering of neutrons by protons in a sample, is given for solids within the one-photon approximation by

$$\frac{d^2\sigma}{d\Omega d\omega} \propto \left(\frac{E_f}{E_i}\right)^{1/2} \frac{q^2}{\hbar\omega} \int_0^T d\tau' \exp(i\omega\tau) \langle \vec{v}(\tau) \cdot \vec{v}(0) \rangle,$$

where the bracketed object is the velocity time autocorrelation function, averaged over all protons in the system. The INS spectrum is a convenient route to the temperature-dependent phonon density of states—a quantity that is very difficult to measure using optical techniques. In this case, the primary input does not explicitly involve the electron density and can, in principle, be calculated with high fidelity using a suitably accurate empirical force field.

We have performed QC/MD simulations of benzene using the TBON code, in which the electronic structure is based on a semi-empirical molecular orbital description of the valence electrons. In traditional tight-binding approaches, where eigenfunctions for the system Hamiltonian are determined, the computational work scales as the cube of the number of atoms *N*. In TBON, a recently developed algorithm that scales linearly with *N* is used to find the electronic states of the system. Such scaling, coupled with an efficient parallel implementation of the algorithm, allows for QC/MD simulations of greater size and length of trajectory in time relative to traditional quantum approaches.

As an example of condensed phase spectra computed from QC/MD, in Figure 1 we compare the simulated inelastic neutron scattering spectra for liquid benzene at room temperature (RT, 300 K) and pressure (density = 0.88 g/cc) versus compressed liquid benzene (density = 1.95 g/cc, pressure = 9 GPa, temperature = 1510 K). Many sharp peaks, for example, C-H stretching (~ 3400 cm^{-1}) and C-C stretching (~ 1000 cm^{-1}), are apparent in the RT spectrum. The 9 GPa spectrum exhibits broadening, relative to the RT spectrum, due to increased collisions between molecules at this elevated temperature and pressure. In Figure 2 we show a molecular dynamics snapshot for the high-pressure, high-temperature case; the simulation contained 54 molecules in a 3-D periodic primary cell.

In the coming year, we plan to use the MondoSCF hybrid density functional theory (DFT) code under development in T-12 and T-14 by Matt Challacombe and co-workers to extend our capabilities in the area of quantum molecular dynamics. This code, which will feature 3-D periodic boundary conditions, O(*N*) computational scaling, and molecular dynamics and Monte Carlo drivers, will enable simulations of thousands—rather than hundreds—of atoms. The hybrid DFT capability, including B3LYP and PBE1 functionals, allows for a more accurate treatment of the electronic structure, relative to the semiempirical molecular orbital methods employed above.

We will simulate thousands of atoms at arbitrary pressures and tempertures using quantum chemistry coupled with molecular dynamics.

jdk@lanl.gov
sewell@lanl.gov
lac@lanl.gov
emk@lanl.gov

This paper is a portion of LA-UR-01-1847, May 2001.